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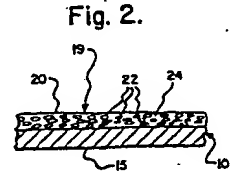
(54) A method of manufacturing a neutron absorbing article and neutron absorbing articles.

(57) A neutron absorbing article, suitable for absorbing neutrons released by spent nuclear fuel stored in a storage rack in a storage pool, to prevent undesirable emission thereof, is made by plasma spraying onto a metal or metal alloy substrate (15) boron carbide and a metal or metal alloy (17), fed to the plasma spray gun (11) in powder form, until a suitable areal density of B^{10} (or a suitable thickness of the boron carbide in a matrix of the metal or alloy) is deposited. Such areal density is usually obtained at a thickness from 3 to 6 mm. and the deposit resulting is hard and strong and may be ground or otherwise machined to desired surface configuration, which is preferably smooth and flat or tubular. The plasma sprayed coating is also usefully applied to various other items, such as spent fuel shipping casks, body shields, vehicle shields, equipment housings and room walls, to prevent passing of neutrons through them.

Fig. 2.



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MANUFACTURE OF NEUTRON ABSORBING ARTICLES

This invention relates to neutron absorbing articles, to methods for their manufacture and to their uses to prevent undesirable emissions of neutrons from sources thereof, such as spent nuclear fuel. More particularly, the invention is of a method for manufacturing such neutron absorbing articles wherein boron carbide and a metal or metal alloy matrix for the boron carbide are plasma sprayed onto a metal or metal alloy substrate, the article made and neutron absorbing uses thereof.

The B^{10} content of boron is known to be an especially useful neutron absorber. Boron carbide has been employed for its neutron absorbing properties and articles containing boron carbide, in metallic and polymeric matrices, have been manufactured and have been successfully employed as neutron absorbers, sometimes in storage racks for spent nuclear fuels, which racks are usually located in aqueous storage pools. Recently various neutron absorbing articles, often in flat plate form, have been made by dispersing boron carbide powder in a phenolic resin matrix and curing the resin, whereby

there is formed a stable article of high neutron absorbing power. Although such articles have been successfully employed as neutron absorbers and have excellent stabilities for most applications, because the phenolic resin is organic there is a possibliity that some decomposition thereof and loss of physical properties may be encountered after lengthy use, e.g., after 20 to 40 years. Also, it is sometimes advantageous for a nuclear absorbing article to be of better thermal conductivity than such articles based on phenolic resin (which has a comparatively low thermal conductivity). It is known that metals are much better conductors of heat than organic polymers and additionally, they are resistant to weakening due to radiation from nuclear materials. For such reasons mixtures of boron carbide and aluminum particles have been encased in aluminum sheaths and have been employed as neutron absorbers and in other instances boron carbide particles have been dispersed in melts of metallic materials which, upon cooling, have been found to be useful neutron absorbing articles.

Flame spraying and plasma spraying of boron carbide have been effected to coat wear parts of machinery and bearings and to form hardened surfaces on tools of various types. In some cases such processes have been suggested for the manufacture of radiation absorbing items. However, it is known that boron carbide may decompose when flame sprayed so as to produce boric oxide, which is objectionable in neutron absorbing articles which could be exposed to aqueous media (due to a leak in a storage rack wall or for other reasons). Also, plasma spraying, as described in

the art known to applicants, is of different materials, effected differently or results in a different product from that of applicants and it is considered that the present products are superior to those of the prior art. For example, it has been reported to one of the applicants that the thicknesses of deposit needed to make most satisfactory neutron absorbing plates (or other shapes) were hitherto unobtainable.

In accordance with the present invention a method of manufacturing a neutron absorbing article comprises plasma spraying boron carbide and a metallic substance selected from the group consisting of metals and metal alloys onto a substrate so that the boron carbide deposits on the substrate in a matrix of the metallic substance without oxidation of the boron thereof, so as to produce a neutron absorber that is stable when exposed to an aqueous pool medium in which racks of spent nuclear fuel are stored with a plurality of such neutron absorbing articles therein to absorb neutrons released by the spent fuel and thereby prevent undesirable neutron emissions therefrom. It is highly preferable for the metal of the substrate to be the same as the metal of the matrix and to be either aluminum, copper or stainless steel, the boron carbide and the matrix metal or alloy to be charged to the plasma gun in powder form, the plasma sprayed deposit to be 70 to 90% by volume of boron carbide and the thickness thereof to be from 3 to 6 mm. Also within the invention are the articles made and uses thereof in spent fuel storage racks and for similar neutron absorbing functions.

The invention will be readily understood from this specification and the drawing, in which:

FIG. 1 is a somewhat schematic representation of the application of boron carbide and matrix metal or metal alloy to a corresponding metal or metal alloy substrate by means of a plasma spray gun;

FIG. 2 is an enlarged vertical section along a longitudinal axis of a portion of a flat plate article made by plasma spraying by the method shown in FIG. 1;

FIG. 3 is a top plan view of the article of FIG. 2;

FIG. 4 is a representation of a top plan view of the article of FIG'S. 2 and 3 after grinding of the plasma spray deposit to a flat surface;

FIG. 5 is a side elevation of an article of this invention with plasma spray deposits on both major surfaces thereof, ground to flat surfaces;

FIG. 6 is an end elevation of a cylindrical tube coated on the exterior surface thereof with a neutron absorbing deposit in accordance with this invention;

FIG. 7 is a transversely vertically sectioned end view of a substrate of this invention before application of a plasma spray deposit thereto;

FIG. 8 is a view corresponding to FIG. 7 but with the plasma spray deposit thereon;

FIG. 9 is a view corresponding to FIG. 8 but with the plasma spray deposit ground down;

FIG. 10 is a perspective view of a spent fuel storage rack containing a plurality of assemblies for storing spent nuclear fuel; and

FIG. 11 is a sectional view taken along plane 11-11 of FIG. 10, illustrating the location of neutron absorbing plates of this invention in the walls of one of the assemblies of the rack of FIG. 10.

In FIG. 1 a suitable plasma spray gun, usually of the Metco or Bay State type, capable of depositing from 2 to 10 kilograms per hour of aluminum (or equivalent weights of other metals), is designated by numeral 11. As shown, the plasma spray gun is held above the work and at an angle to it, with the work passing in the direction of arrow 13 and the gun being moved reciprocatingly transversely with respect to the work. The work or substrate 15, of a suitable material, such as a metal or metal alloy, e.g., aluminum, copper or stainless steel, has a mixed plasma spray 17 applied to it to form a coating 19 of boron carbide distributed evenly throughout a metal matrix. In the plasma spray gun a mixing chamber 21 is shown schematically, in which boron carbide particles and metal or metal alloy particles, preferably with the metal or metal alloy being the same as that of the substrate, are mixed together before addition through passageway 23 to the plasma stream. Inlets and outlets for the plasma gas and electrical connections are not shown in the schematic view of the gun nor are holding and moving means illustrated because such are well known in the art. As will be noted, the surface 20 of deposit 19 is not perfectly regular, due to the method of laying down the B_4C - matrix plasma coating.

In FIG. 2 particles 21 of boron carbide are shown in greatly exaggerated form distributed evenly throughout metal matrix 23 of coating 19. Although not exactly illustrated in the figure the boron carbide particles preferably are from 70 to 90% by volume of the coating. In FIG. 3 the "rippled" or "weld-type" nature of the deposit is indicated, with the rippled surface being designated by numeral 25. In FIG. 4 such

surface is shown ground flat as surface 27 of absorber 10'. In FIG. 4 boron carbide particles at such surface are not shown but it will be understood that in grinding the surface down or otherwise smoothing it by removal of material at least some of the boron carbide particles will be exposed unless such surface is previously covered with a layer of the matrix metal, preferably by plasma spraying thereof, which is subsequently smoothed without cutting the carbide particles.

In FIG. 5 another form of the invention is illustrated wherein the neutron absorbing coating is applied to two sides of a substrate material. As shown, neutron absorber 29 includes substrate 31 coated on both major surfaces thereof with boron carbide-substrate material coatings 33 and 35, both of which are shown as smooth surfaced, although the surfaces thereof may also be like those of absorber 10, as in FIG'S. 1-3. FIG. 6 illustrates a cylindrical or tubular substrate 37 having a neutron absorbing coating 39 on the exterior thereof, to form cylindrical neutron absorbing article 41.

In FIG. 7 substrate 43 has a longitudinal cavity therein defined by side walls 45 and 47 and bottom wall 49. In FIG. 8 such cavity is filled with a plasma sprayed coating 51 of boron carbide particles in matrix material to form neutron absorber 53 and in FIG. 9 neutron absorber 53' is shown wherein the extended surface 52 of the absorber of FIG. 8 has been machined away to produce a smooth surface 54.

As is shown in FIG'S. 10 and 11, spent fuel rack 55 includes sixteen assemblies 57, each of which is of essentially square cross-section and each of which includes an outer wall 59, an inner wall 61 and

intermediate such walls and enclosed between them, tops 63 and bottoms, not illustrated, which seal off each of the assemblies about the contents, neutron absorbing plates 10'. Inside the assemblies of the rack are stored the spent nuclear fuel rods, not specifically illustrated herein, which extend vertically through the assemblies and have access at the ends thereof to water or aqueous solution in a pool or suitable container, not illustrated, in which the racks are stored. The assemblies of the rack are welded together and are supported on a bottom member 65, mounted on legs 67, which are adjustable in height to permit leveling of the rack. As is seen in FIG. 11, neutron absorbing plates 10', which are of uniform width, height and thickness, are slid into place between vertical rods 69, which are welded to the inner and outer walls 61 and 59, respectively.

The plasma spray gun may be any such gun of types known in the art which are capable of feeding a mixture of powders to an argon or other inert gas plasma and of spraying these at supersonic velocities onto substrate surfaces held near to them. For example, a Metco type 2MB plasma spray gun may be employed, using a B nozzle but in the present experiments a comparable gun made by Bay State Abrasives Co. is used. The plasma gas flow and other conditions may be adjusted to obtain an effective plasma. For example the gas flow is adjusted to within a range of 100 to 5,000 liters per hour, preferably 2,000 to 4,000 l./hr. at standard conditions, with the pressure being in the range of 1 to 7 kg./sq. cm., preferably 2 to 5 kg./sq. cm. The voltage is set to from 50 to 250, preferably

60 to 100 and the electric current flow is from 200 to 600, preferably 300 to 500 amperes. The spray distance is 5 to 15 centimeters, preferably being from 7 to 12 cm. The gun is inclined at an angle of 30 to 60°. It will normally be capable of depositing from 2 to 10 kilograms per hour of aluminum, preferably 5 to 10 kg./hr. thereof or equivalent amount of other metal, for example, from 4 to 20 kg./hr. of copper or of stainless steel. The presence of the boron carbide affects the gun capacity about as if it were aluminum.

The substrate to which the plasma spray is applied is normally a metal or metal alloy but it is within the concept of this invention to apply such spray to other suitable substrates which possess the desirable chemical and physical properties to make them useful in neutron absorbing articles intended for employment in storage racks for spent nuclear fuel. Thus, it is possible that such substrate could be a phenol formaldehyde polymer or other suitable polymeric material or it might be a natural material, such as certain hardwoods or composites made from them and a polymeric binder. Alternatively, mineral and other inorganic materials dispersed in a suitable binder can be employed. However, the use of organic substances is not preferred due to their possible deterioration over a period of use of the neutron absorber and similarly, the employment of mineral materials sacrifices thermal conductivity, which is an important advantage of metal or metal alloy-based substrates. Various metals may be employed and without prejudice to the use of other metals, such as iron, steel, magnesium, and other alloys, such as brass and bronze, all of which are

satisfactorily conductive and which may be coated by the method of this invention, it is highly preferable to utilize aluminum, copper or stainless steel. Further to avoid electrochemical or galvanic reactions it is preferred that the substrate be of the same composition as the matrix material being applied to it (and the storage rack in which the absorber may be used). The thicknesses of the substrates and their shapes may vary but normally, as for a plate or tubular absorber to be coated with neutron absorbing material in a metal or alloy matrix, the thickness will be from 1 to 10 mm., preferably from 2 to 5 mm. It is usually desirable to employ comparatively thin substrates so as to keep the costs, thickness dimensions and weights of the finished articles as low as feasible. Thus, in addition to saving money there will be savings in structural supports for the storage racks or other apparatuses employed and it will be possible to have more racks in a given volume and to have them of greater neutron absorbing capabilities when the substrate thicknesses are kept low. Although flat plate and tubular, especially rounded corner square tubes, are those much preferred as substrates for the neutron absorbing coatings of this invention, the substrates may be of other shapes too and may be made so that they can be bent to or assembled to desired shapes after manufacture. In this respect it is to be noted that, probably due to the high boron carbide contents of the neutron absorbing articles, they are not readily formable by bending after manufacture, so it is desirable for an uncoated substrate portion to be intermediate coated portions for bending along such uncoated surface to

form other shapes of the final neutron absorbing article. Thus, bending can be effected without adversely affecting the boron carbide-matrix deposit on the substrate. Alternatively, the plasma spray may be deposited on items previously shaped, e.g., body armor, room walls, machine shields, equipment protective devices, live or spent nuclear fuel shipping casks, etc., which may be of thicknesses within the range previously given or greater than such thicknesses, as befits the particular application.

The boron carbide powder employed may be a commercial boron carbide which is low in boric oxide or other boron oxides, chloride and iron. Normally the chloride or other soluble salt content will be essentially nil, the iron content will be 3% or less, preferably 2% or less, more preferably 1% or less and most preferably will be less than 0.5%, with the B_2O_3 (or other boron-oxygen compound, considered as a B_2O_3 equivalent) content being no more than 2%, preferably less than 1%, more preferably less than 0.5% and most preferably less than 0.2%. The lower the iron and B_2O_3 contents the better. The percentages mentioned are those in the boron carbide (B_4C) charged and in the deposit on the substrate (neglecting the metal or metal alloy matrix). Thus, the boric oxide content will be limited to the percentages mentioned, based on the boron carbide present. It has been found that in plasma spraying with an inert gas and without the presence of combustible materials and oxygen present there may be a reduction in the boric oxide content of the boron carbide powder so that the final product is lower in B_2O_3 than the powder charged. However, the important thing is that in the plasma spray operation

no additional boric oxide is formed from the boron carbide, which may be the case with other high temperature and high velocity applications and methods, such as flame spraying. The particle sizes of the boron carbide and matrix materials will usually be such that substantially all (over 90%, preferably over 95% and more preferably over 99%) passes through a No. 170 U.S. Sieve Series screen and at least 50% passes through a No. 200 screen. Preferably the particle sizes are in the 20 to 200 micron range, more preferably in the 30 to 100 micron range. Spherical or nearly spherical particles are preferred for their ready miscibility and flowability. The purities of the metals or metal alloys utilized are generally 99% or more, preferably at least 99.5% and more preferably at least 99.9%. The boron carbide and metallic material particle sizes may be chosen to obtain the desired boron carbide particle size in the finished coating and to promote best bonding of the metallic material matrix to the boron carbide. In this respect it is considered that the finer the particle size the better for most applications providing that good flow and plasma melting of the particles are obtained (at least of the matrix).

Application of the plasma spray to the substrates may be by relative movement of the plasma gun and the substrate, either with the gun or the substrate moving or with both moving. Normally such application approximates that of paint spraying, with care being taken to evenly distribute the coating on the substrate. Pluralities of coating layers may be employed and it is a feature of this invention that due to the excellent bonding of the plasma spray to the

substrate and due to excellent bondings of subsequent sprays to previously deposited sprays, considerable thicknesses of the coating may be produced without bonding failure despite relatively minor proportions of matrix or binding material being utilized. In this respect, it is noted that it will usually be desirable to employ as much of the neutron absorbing boron carbide as is feasible and it has been found that in utilizing the metals and alloys mentioned one can deposit from 70 to 90% of boron carbide in the coating (by volume). Generally such comparatively high concentration of boron carbide will be preferred but in some instances only a major proportion of boron carbide will be present (50 to 90%). It is possible to utilize more metal or metal alloy so that the percentage of boron carbide may be below 50%, down to 20% and such may be desirable with particular substrates and matrix materials which may not sufficiently hold the boron carbide particles in the matrix at higher boron carbide concentrations. At such lower B_4C "concentrations" the physical characteristics of the product are more like those of the substrate and matrix metal(s). However, it is a feature of this invention that the higher concentrations can be obtained in the present articles, thereby allowing them to be made of lesser thicknesses while still being effective. Of course, substrate thickness will be maintained sufficient to make the product form-retaining so that it will not inadvertently be bent, causing cracking off of the coating.

The thickness of boron carbide-matrix coating, in which it is found that the boron carbide particles are very uniformly distributed, will normally be such that the B^{10} content thereof is that specified by the electric utility or other operator of the spent fuel

storage pool or other facility or application in which neutron emission is to be controlled. Because such specification will normally be in the range of 0.01 to 0.1 g./sq. cm. of B^{10} the thickness of the coating should usually be at least 0.5 mm. and preferably will be 3 to 6 mm., being 3 to 5 mm. after grinding or other surface removal of excess of coating to smooth such surface. Incidentally, such removal, in addition to being effectable by grinding, may also be accomplished by sonic and electrical discharge processes, among others. When, as in FIG. 5 both sides of the matrix are coated,one can further increase the neutron absorbing capability or can diminish the individual coating thicknesses while still having sufficient neutron absorbing power to satisfy specifications. It is within the present invention to effect coatings on both sides of an article simultaneously, in which case application rates can be doubled. It is also within the invention to apply the present coatings to both sides of cylindrical or tubular containers to make a modification of the coated cylinder of FIG. 6.

In many uses of the present invention it may be unobjectionable to use an article having the distinctive plasma ripples on the coating surface and if such is possible it will often be preferred. Use of the item as made avoids additional operations and allows the retention on the surface of a coating of the matrix metal or alloy, thereby preventing contact of the boron carbide with external materials and the atmosphere. Also, as was indicated previously, one can further coat, as by plasma spraying, matrix material over the boron carbide-matrix deposit and then machine such down

to final desired dimensions without cutting the boron carbide particles, thereby leaving a protective coating of matrix over them. However, such involves an additional operation and an additional expense and therefore very often it will be desirable to avoid it. Because of the inert nature of the boron carbide to various media, providing that little or no boric oxide is present therein, it will often be possible to machine down the surface of the coated article, as by grinding, to produce a more regular surface than is obtainable by plasma spraying. Such machining can be effected simultaneously on both sides of an article to produce a flat plate like that of FIG. 5.

To facilitate the production of coated product to specification dimensions articles like that of FIG. 9 may be made by the method previously described, so that the exact amount of coating mixture is known to be in place. If desirable, the substrate containing the cavity may contain cavities adjacent to both major surfaces thereof and coating material may be applied in both such cavities, after which it either may or may not be machined to final dimensions. In addition to promoting the obtaining of known quantities of neutron absorber in the neutron absorbing article the walled cavities shown in FIG'S. 7-9 also help to stabilize the coating, protecting it from being dislodged or having its bonding to the substrate weakened by lateral blows. Similarly, transverse walls in the substrate may be utilized so that greater lengths, e.g., one meter, or more of deposit, are not made without a reinforcing substrate divider between them. In addition to using the illustrated vertical walls, the walls of the cavity

may be undercut to promote holding of the coating. To "protect" the boron carbide the deposit may be coated with matrix metal after grinding to be even with the substrate surface, and excess matrix may then be machined off to produce a smooth surface.

In use, the present neutron absorbers, in plate form, may be made as long as 2 to 7 meters, providing that the substrate is sufficiently strong so as to maintain its shape without undue bending, but preferably plate lengths will be from 0.5 to 2 meters, e.g., 1.5 meters. The plates may be stacked one atop another and a plurality of plates may be employed within the walls of a storage rack assembly. The present articles, having very hard and comparatively smooth (and sometimes extremely smooth) surfaces, may be easily slid in and out of position without removing significant amounts of boron carbide particles, which can occur when the boron carbide particles are not as well covered by the matrix material as in the present products. It is considered that the useful lives of the present absorbers, whether ground or unground at the coated surfaces, will exceed those of other nuclear absorbers presently in use because the coatings are so coherent and are so firmly held to the substrates and because the metals and alloys do not deteriorate during use due to radiation effects. Tests made on the articles of this invention indicate that they are superior to all other neutron absorbers presently in commercial use. Furthermore, the manufacturing method lends itself to automation and to the speeding up of application techniques by the utilization of a plurality of plasma spray guns at one time coating a particular work. The same plasma gun, preferably equipped with adjustable feeding devices for the powders, can be used to spray various mixes of B_4C

and metallic material or the metal or alloy alone, without the need for changing guns or remounting the plasma gun. Deposit thickness adjustments can be readily made, if desired. Initial special preparation of the powder charged to the plasma spray gun or supplying the charge as a rod is unnecessary and manufacturing costs are expected to be capable of being lowered so as to make them cheaper for the present products than costs for making other comparable neutron absorbers.

In use in a fuel storage rack, as illustrated in FIG'S. 10 and 11, the neutron absorbing article is positioned with respect to a neutron emitting source so as to absorb neutrons emitted from it and prevent them from passing out of the storage area to areas where they might be damaging to personnel or equipment. They may be similarly employed in other neutron absorbing applications. When used in a spent fuel storage rack containing spent fuel (the racks of FIG'S. 10 and 11 may be considered as containing such fuel in the central portions thereof) the absorbers will be located so as to prevent release of neutrons past them. Thus, where the boron carbide-matrix deposition is interrupted, as in the articles of FIG'S. 7-9 and in similar products containing transverse walls about the illustrated cavities, the articles will be staggered or otherwise positioned so that the effective neutron absorbing coating will surround the spent nuclear fuel, preventing any escapes of neutrons through the substrate walls.

The following examples illustrate but do not limit this invention. Unless otherwise indicated all parts are by weight and all temperatures are in °C.

EXAMPLE 1

A flat strip of aluminum, about 8 cm. wide, 25 cm. long and 3 mm. thick is degreased, utilizing standard degreasing equipment, and is then roughened on a major surface thereof by sand blasting, again using standard equipment. Areas to which the plasma sprayed coating is not to be applied are masked before sand blasting, using multiple layers of standard masking tape. Such tape may be removed or left on while plasma spraying onto the roughened surfaces. A boron carbide powder containing less than 0.5% of boric oxide and of 260 mesh (No. 260, U.S. Sieve series), corresponding to a particle size of 20 to 55 microns, and a standard aluminum plasma spray powder of a particle size in the 30 to 75 micron range are weighed out in desired proportions, 25, 50 and 75% by volume of boron carbide), placed in the mixing and feed unit of the plasma spray gun, which is a Bay State Abrasives Co. (Division of Avco Corporation) gun of the type previously described, and the composite mix is plasma sprayed, employing typical known and established conditions for the aluminum matrix metal being employed, which conditions were previously mentioned. In the spraying operation the substrate is maintained stationary and the gun is moved transversely and backwardly with respect to it so as to apply the coating as uniformly as possible in an operation simulating spray painting. Repetitive passes are made, keeping the gun continually moving, with each pass overlapping the previous one. Plasma spraying is stopped when the desired thickness is achieved. In the coating of the aluminum substrate with aluminum and boron carbide the thicknesses deposited range from 0.4 mm. to 4 mm.

The products made are all useful as neutron absorbers except that those containing only 25% (even 50%) B_4C are not nearly as satisfactory as the 75% product, which is decidedly superior. All the deposits made are firmly held to the substrate and are of high strength. However, they can be cracked off the substrate by excessive bending thereof although limited bending is possible without adversely affecting their properties. In this respect the 25% B_4C product is less susceptible to such cracking.

EXAMPLE 2

The experiment of Example 1 is repeated but instead of utilizing aluminum, copper particles and substrate are employed, with the weight percentages of the particles being increased so as to maintain the volume percentages the same as previously described. Also, the gun firing conditions, the argon feed, etc., are adjusted for best establishment of the plasma. Coatings of the thicknesses mentioned in Example 1 are applied and the products are examined and, like those of Example 1, appear to be strong, firmly adherent and uniform, suitable for use as neutron absorbers. However the 75% B_4C product is most preferred, with the 50% product being considered to be next best as a neutron absorber.

EXAMPLE 3

The experiments of Examples 1 and 2 are repeated, using 304 stainless steel powder and substrates instead of those of aluminum and copper. The weight of the stainless steel powder used is essentially the same as that of the copper. The coatings deposited are of the same thicknesses as those previously described

and the articles appear to have the same type of properties. Other stainless, e.g., 317, 318, may also be used.

EXAMPLE 4

The products of the previous examples are subjected to grindings to smooth the coated surfaces, as shown in FIG. 4. Such grindings (and other surface smoothing methods may be employed, too) do not adversely affect the adherences of the coatings to the substrates.

EXAMPLE 5

Products like those of FIG'S. 5 and 6 are made by plasma spraying the compositions previously described in Examples 1-3 onto the indicated surfaces to make useful neutron absorbing articles. In a variation of this experiment the exteriors of square cross-section and rounded square cross-section tubes are so sprayed to produce a neutron absorbing tube which can be fitted about the neutron emitter in place of the inner walls of and absorber plates of the assemblies of FIG'S. 10 and 11.

EXAMPLE 6

The substrates utilized are modified, as shown in FIG'S. 7-9, and "75%" B_4C deposits in matrices of Al, Cu and stainless steel are applied, as in Examples 1-3. The articles made are useful neutron absorbers.

EXAMPLE 7

The products described in the foregoing examples are employed in absorbing neutrons generated by a neutron releasing material, such as spent nuclear fuel, in a fuel storage rack in a storage pool, which pool is filled with a normal aqueous storage pool

medium containing boric acid. The neutron absorbers operate effectively and when tested against the pool medium are found not to corrode objectionably. In such uses, to avoid galvanic corrosion or electrochemical interactions, the substrates and matrices employed in the neutron absorbing articles are of the same metals as those of the storage racks.

EXAMPLE 8

The coatings of the previous examples are applied to various other substrates, preformed or to be formed subsequently, and are applied interiorly, exteriorly, about curves, about angles and in such curves and angles, and the coatings made firmly adhere to the surfaces of the substrates, which are of the same materials as the coatings, and are useful as neutron absorbers. When, in this example and the other examples, the substrates are of different metals or alloys from the matrix of the coating, firm adherences are obtained and good products are made but there is some danger of galvanic corrosion, especially over long periods of time and if the absorber should be exposed to water or a humid atmosphere.

In the preceding examples one can use "diluent" refractory materials with the boron carbide, such as silicon carbide, if desired and also, some of the boron carbide (or all, with less desirable results) may be replaced with other neutron absorbers, e.g., boron nitride, and useful products result. However, this invention is directed primarily to making a superior neutron absorber based on boron carbide.

The invention has been described with respect to various examples and illustrative embodiments

thereof but is not to be limited to these because it is evident that one of skill in the art with the present specification and drawing before him will be able to utilize substitutes and equivalents without departing from the invention.

WHAT IS CLAIMED IS:

1. A method of manufacturing a neutron absorbing article which comprises plasma spraying boron carbide and a metallic substance from the group consisting of metals and metal alloys onto a substrate so that the boron carbide deposits on the substrate in a matrix of the metallic substance without oxidation of the boron thereof, so as to produce a neutron absorber that is stable when exposed to an aqueous pool medium in which racks of spent nuclear fuel are stored with a plurality of such neutron absorbing articles therein to absorb neutrons released by the spent fuel and thereby prevent undesirable neutron emissions therefrom.

2. A method according to claim 1 wherein the boron carbide and the metallic substance are fed to the plasma as powders, the metallic substance is selected from the group consisting of aluminum, copper and stainless steel, the substrate is of the same metallic substance as that of the powder, the percentage of boron carbide in the plasma sprayed deposit is from 50 to 90% by volume and the thickness of the plasma sprayed deposit is at least 0.5 mm.

3. A method according to claim 2 wherein the boron carbide and the metallic substance particles are pre-mixed before addition to the plasma, the particle sizes thereof are in the range of 20 to 200 microns, the boron carbide is from 70 to 90% of the deposit, by volume and the thickness of the deposit is from 3 to 6 mm.

4. A method according to claim 3 wherein the substrate is degreased and ground before plasma spraying the deposit onto it, the deposit is that resulting from a series of passes of a plasma spray gun with respect to the substrate and the surface of the deposit is ground to desired shape.

5. A method according to claim 4 wherein prior to deposition the substrate is formed with a cavity therein, the deposit is applied to fill such cavity and project beyond a surface of the substrate and the deposit beyond such surface is ground off.

6. A method according to claim 5 wherein the neutron absorbing article is in flat plate form and the thickness of the deposit after grinding is from 3 to 5 mm.

7. A method according to claim 3 wherein the application of the plasma spray is to a square cross-section tubular substrate.

8. A method according to claim 6 wherein the plasma is an argon plasma.

9. A neutron absorbing article which comprises a substrate of a metallic substance selected from the group of metals and metal alloys having bound to a surface thereof a plasma sprayed deposit of boron carbide in a matrix of a metallic substance selected from the group of metals and metal alloys in which the content of boric oxide is less than 1% of the boron carbide.

10. An article according to claim 9 wherein the substrate and the matrix metallic substances are the same and are selected from the group consisting of aluminum, copper and stainless steel, the proportion of boron carbide in the plasma sprayed deposit is from 50 to 90% by volume thereof and the thickness of the deposit is at least 0.5 mm.

11. An article according to claim 10 wherein the boron carbide is uniformly distributed in the plasma sprayed deposit and is 70 to 90% thereof by volume and the thickness of the deposit is from 3 to 6 mm.

12. An article according to claim 11 wherein the surface thereof is ground and smooth.

13. An article according to claim 12 wherein the substrate includes a cavity filled with plasma sprayed deposit, the surface of which deposit is ground smooth and continuous with a surface of the substrate.

14. An article according to claim 13 in flat plate form with the thickness of the plasma sprayed deposit after grinding being from 3 to 5 mm.

15. An article according to claim 14 wherein the boron oxide content is less than 0.5% of the boron carbide.

16. An article according to claim 10 which is in flat plate form.

17. An article according to claim 10 which is in tubular form.

18. A neutron absorbing article according to claim 9 positioned with respect to a neutron emitting source so as to absorb neutrons emitted therefrom.

19. A spent fuel storage rack containing spent fuel and a plurality of neutron absorbing articles according to claim 12 positioned about said spent fuel so as to absorb neutrons emitted by it and prevent the undesirable escape thereof.

20. A nuclear product shipping cask comprising a neutron absorbing shielding article according to claim 9.

Fig. 1.

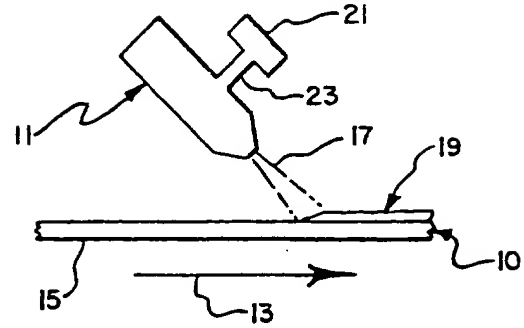


Fig. 2.

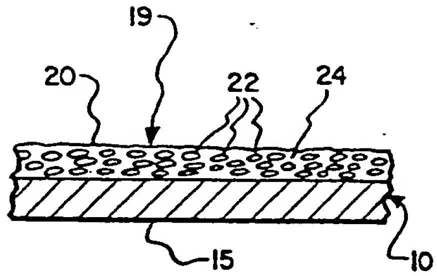


Fig. 3.

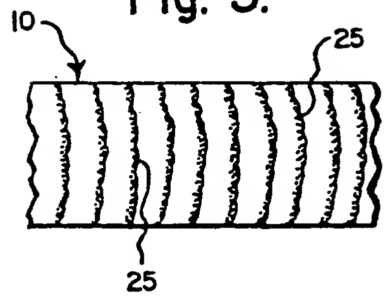


Fig. 4.

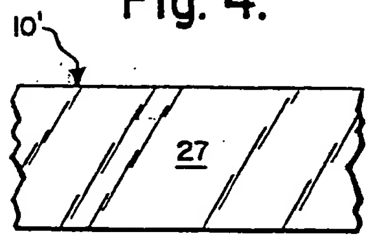


Fig. 5.

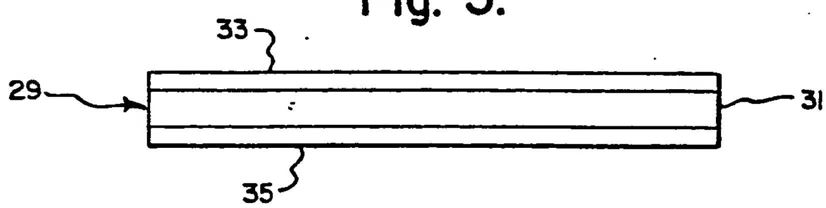


Fig. 6.

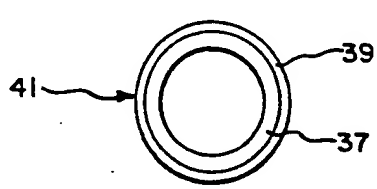


Fig. 7.

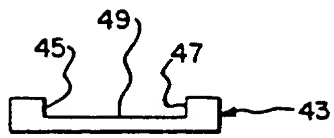


Fig. 8.

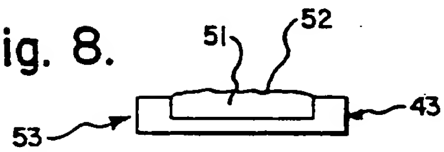


Fig. 9.

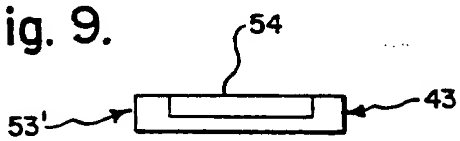


Fig. 10.

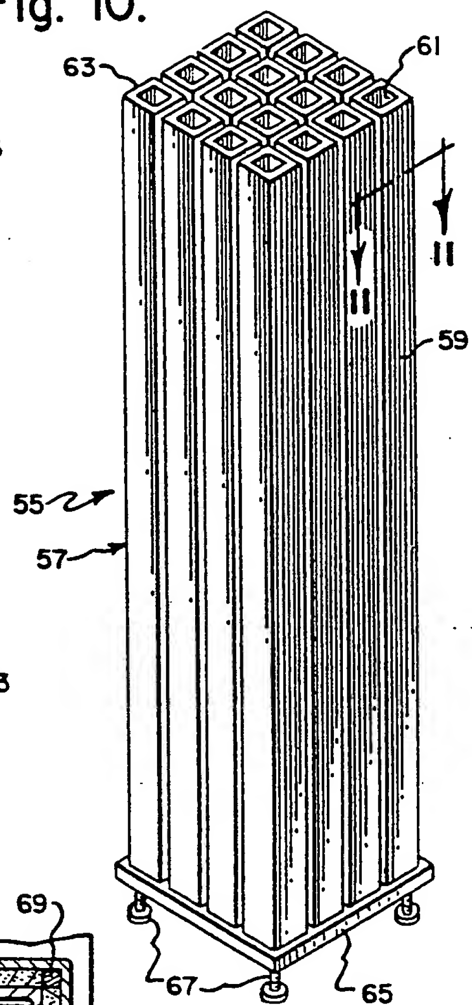
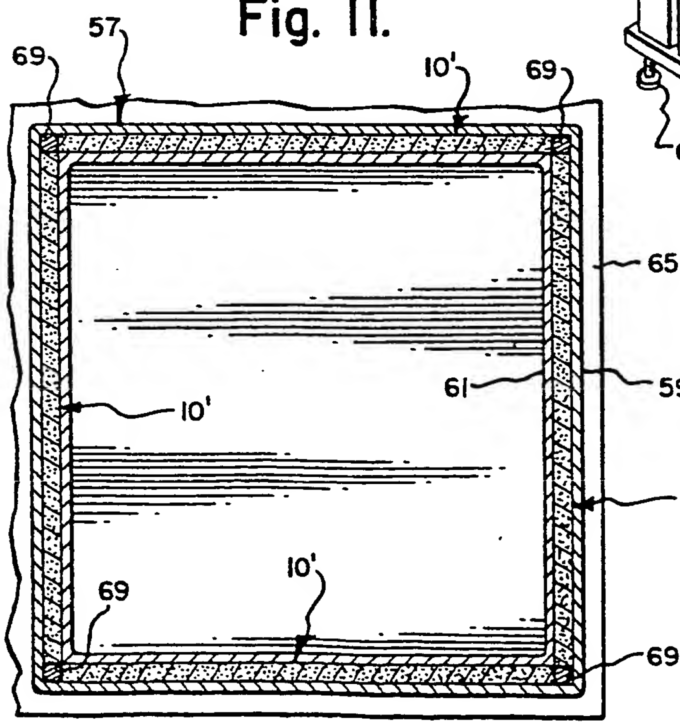


Fig. 11.



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EUROPEAN SEARCH REPORT

0016252
Application number

EP 79 10 4502

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	FR - A - 1 252 868 (PAGANELLI) * Abstracts 1,2,5 *	1,3,16 19
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	GB - A - 1 075 655 (NORTON) * Claims 1,7,9; page 3, lines 113-123 *	1,8,10
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	US - A - 2 727 996 (ROCKWELL) * Claims 1,2,4,9 *	1,2,10

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

G 21 F 1/08
C 23 C 17/00

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

G 21 F 1/08

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	30-05-1980	NICOLAS

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